

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

N-63-4-2

ASD-TDR-63-290

408084
CATALOGED BY DDC
AS AD No. 403084

The Spectrochemical Determination of Boron in Molybdenum

James H. Muntz

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-290

April 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

100
JUN 17 1963
DESC
TISA A

Project No. 7360, Task No. 736005

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C., in stock quantities for sale to the general public.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

FOREWORD

This report was prepared by the Physics Laboratory. The work was initiated under Project 7360, "Materials Analysis and Evaluation Techniques," Task No. 736005, "Compositional, Atomic, and Molecular Analysis." It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with James H. Muntz acting as project engineer.

This report covers work conducted from October 1962 to February 1963.

The chemical analyses referred to in table 3 were performed by K. F. Sugawara.

ABSTRACT

A method for the spectrochemical determination of boron in molybdenum is described. The method provides for the determination of boron in the 50 to 500 ppm range by a carrier-distillation technique with a precision of ± 10 per cent.

This technical documentary report has been reviewed and is approved.



FREEMAN F. BENTLEY
Chief, Analytical Branch
Physics Laboratory
Directorate of Materials and Processes

TABLE OF CONTENTS

	Page
INTRODUCTION	1
APPARATUS	2
PROCEDURE	2
DISCUSSION	3
LIST OF REFERENCES	8

INTRODUCTION

Currently an internal research program is being conducted by the Physical Metallurgy Branch, Metals and Ceramics Laboratory, Directorate of Materials and Processes to study the effects of selected grain refining additions on the structure of molybdenum and other refractory metals and alloys. One major difficulty in processing refractory metals has been the coarse columnar structure present in the as-cast ingots. Nucleation methods have produced fine-grained equiaxed cast structures in other alloy systems. It was predicted that certain borides would be the most effective nucleating compound for the systems under investigation, and the addition of boron and boron compounds was studied. The cast ingots were to be evaluated by macrosection examination, correlation of measured average grain diameters with boron content, and correlation of fabricability. Since there have been no methods published for the spectrochemical determination of boron in molybdenum, it was necessary to develop a method in order to analyze these materials for boron content.

The spectrochemical determination of boron in molybdenum presents two major problems. The first problem involves the complex spectrum and intense continuum produced when molybdenum is arced. The second involves the possible loss of boron if chemical treatment of the sample is necessary. Also to be considered in any spectrochemical method is the problem of obtaining standards that correspond to the sample to be analyzed. The first problem is common in the analysis of any material that has a complex spectrum. Line interference and intense background make the determination of impurities in these materials difficult. To overcome this problem either the impurities must be separated from the matrix or a technique which will depress the matrix spectrum without depressing the spectra of the impurity elements must be used. An example of the first approach is the technique of Anderson (ref 1) which removes the base metals of iron and nickel alloys by use of a mercury cathode. Examples of the second approach which might be applicable to the problem are (a) the technique of Dyck and Veleker (ref 2) in which the refractory molybdenum carbide is formed in the arc, this depresses the molybdenum spectrum but enhances the more volatile impurities, and (b) the technique of Paterson and Grimes (ref 5) where the impurity elements of interest are converted to a very volatile form, in this case fluorides of boron and silicon. The method described follows somewhat the technique of Paterson and Grimes. This approach was favored due to the simplicity and convenience of the sample and standard preparation. Sodium fluoride was used since the low excitation potential of sodium tends to keep the temperature of the arc down helping to reduce the excitation of the molybdenum.

In the chemical treatments necessary in preparing the molybdenum for this technique the second problem, the possible loss of boron, must be considered. Feldman (ref 3) studied the loss of boron when an acid solution was evaporated and its control by the use of mannitol. However, acids that are usually used to dissolve molybdenum will destroy mannitol during evaporation. Mürau (ref 4), in his study on the dissolution of tungsten by hydrogen peroxide, made comparison tests on molybdenum which indicated its rapid dissolution. From these considerations the following sample treatment was developed: Dissolve the molybdenum in hydrogen peroxide, maintain the volume while expelling

the excess hydrogen peroxide, and finally complex the boron with mannitol to prevent its loss. In this treatment no strong acid is used, and the hydrogen peroxide can be eliminated so that the mannitol will not be destroyed. Also, according to Feldman, boron is not lost until the volume is reduced to 2 to 3 ml, so by maintaining the volume at 10 ml no loss should occur while the hydrogen peroxide is expelled.

The method involves two phases, the preparation phase where the volatility of the boron is carefully kept at a minimum to prevent its loss and the second or excitation phase where the boron volatility is purposely increased to enhance its spectrum.

APPARATUS

Bausch and Lomb dual grating spectrograph with illuminator external optics.

National Spectrographic Laboratories arc-spark stand.

Jarrell-Ash Co. Varisource d-c arc portion.

National Spectrographic Laboratories comparitor-densitometer.

Applied Research Laboratories photo processing equipment.

Crescent Dental Mfg. Co. "Wig-L-Bug" amalgamator.

PROCEDURE

Sample preparation - Place 100 mg of molybdenum chips in a 30 ml polyethylene beaker. Add approximately 10 ml of distilled water, 2 ml of 30% H_2O_2 , and warm to effect dissolution. Maintain the volume at approximately 10 ml by periodically adding water while heating to expel the excess hydrogen peroxide. After the hydrogen peroxide has been driven off, add 50 mg of mannitol and take to dryness. Do all heating on a water bath. Remove the residue from the beaker and place in vial with a $\frac{3}{8}$ inch diameter plastic ball. Grind with the Wig-L-Bug for 30 seconds. Mix 100 mg of the residue with 50 mg of graphite (100 mesh) and 7.5 mg of NaF for 30 seconds in a vial but without the plastic ball. Weigh duplicate charges of 10 mg, place in the electrodes, and pack with a $\frac{1}{8}$ inch diameter graphite rod.

Preparation of standards - Place 100 mg of boron free molybdenum in each of five 30 ml polyethylene beakers. Add aliquots of 0, 1, 2, 4, and 10 ml of a solution containing 5 micrograms of boron per ml (as boric acid), and enough distilled water to make the volume approximately 10 ml. Add 2 ml of 30% hydrogen peroxide and continue as for sample preparation. This provides four standards with 50, 100, 200, and 500 ppm boron in molybdenum and a "blank."

Electrode system - Use a $\frac{3}{8}$ inch diameter "necked" electrode with a $\frac{1}{8}$ inch diameter by $\frac{3}{8}$ inch deep cup for the sample (Ultra Carbon Corp. 105-D is adequate) and a $\frac{3}{8}$ inch diameter rod $1\frac{1}{2}$ inches long pointed on one end with a pencil sharpener for the upper counter electrode. Make the sample the anode.

Excitation - Arc the sample and the standards using the conditions listed in table 1.

TABLE 1
EXCITATION CONDITIONS

Direct current arc	230 volts, 7 amps (short circuit)
Grating	30,000 lines/inch
Emulsion	SA-1 spectrographic plate
Filter	25% neutral filter
Analytical gap	3 mm
Spectral region	2400 to 3400 A 1st order
Slit width	0.01 mm
Slit length	2.5 mm
Exposure time	20 seconds

Photographic processing - Process the plate using the following conditions:

Develop - 3 minutes in D-19 at 68°F

Shortstop - 20 seconds

Fix - Kodak Rapid Fixer 2 minutes

Wash - 10 minutes with running water

Dry - Remove excess water with chamois and dry under hot air for 2 minutes.

Photometry and calibration - Photometer the 2496.78 A boron line and convert the transmittance values to intensities using an emulsion calibration curve derived from the two step method. Prepare the analytical curve by plotting intensities versus concentrations for the standards. Obtain the concentration of boron in the sample by relating the intensity to the analytical curve. Figure 1 shows a typical analytical curve.

DISCUSSION

Moving plate studies indicated that, with the matrix used and in the concentration range of 50 to 500 ppm, boron was completely volatilized in 20 seconds. For much higher concentrations, longer arcing is necessary but not practical since the intensity of the molybdenum spectra begins to increase markedly after 25 seconds. To extend the range to higher concentrations it is necessary to dilute the sample with the "blank" material. A lower range can be obtained by using the stronger boron line 2497.73 A and removing the neutral filter.

TABLE 2
REPRODUCIBILITY
PPM BORON

<u>DETERMINATIONS</u>		<u>RUNS</u>	
Determination No.		Run No.	
1	180	1a	245
2	165	b	255
3	165	2a	285
4	160	b	255
5	165	3a	255
6	160	b	265
7	155	4a	295
8	150	b	265
9	165		
10	160		
Average	163		265
Relative Standard Deviation	4.9%		6.5%

Trials with molybdenum and tin as possible internal standards gave results that were more variable than when only the intensity of the boron line was used. This was probably due to the difference in the volatility of these elements and boron in this matrix. Further attempts to find an element of similar volatility were not made since the reproducibility of the method was considered adequate without the use of an internal standard. The precision of the method is indicated by the data presented in table 2. Listed under "Determinations" are 10 values obtained for the same prepared sample, showing the reproducibility of the arcing procedure. Values listed under "Runs" represent the results obtained from duplicate determinations of a sample prepared four times. This shows the reproducibility of the sample preparation. Table 3 gives the comparison between wet chemical and spectrochemical values. Although there is as much difference as 100% between wet chemical and spectrochemical results on one sample, the values are of the same order of magnitude and, since higher, indicate that there was probably no loss of boron by this technique of sample preparation.

To determine if added boron could be recovered, 50, 100, and 150 ppm boron were added to a metal sample. The sample was dissolved and processed in the usual manner. Another study was made to determine if all the boron in the sample was being dissolved and recovered in the residue. To accomplish this the appropriate amounts of metal chips from a sample and the boron free metal were mixed to prepare 0, 25, 50, 75, and 100% with respect to the sample. The chips were dissolved and processed. The results obtained from these two studies are given in table 4 and indicate that the recovery is within the precision of the method.

A preliminary test with tungsten indicated the possible application of this technique for the determination of boron in this metal also.

TABLE 3
COMPARISON OF SPECTROCHEMICAL AND WET CHEMICAL ANALYSIS

Sample No.	PPM BORON	
	Wet Chemical	Spectrochemical
1	163	169
2	282	265
3	73	115
4	54	110
5	1728	1850 ¹
6	330	430
7	451	460
Bottom	17	<10
Top	285	330

¹ This sample was diluted to bring it within the concentration range of the method.

TABLE 4
RECOVERY STUDIES
PPM BORON

	<u>Found</u>	<u>Theoretical</u>	<u>%</u>
Sample	161		
Sample + 50	200	211	95
Sample + 100	269	261	103
Sample + 150	322	311	104

<u>% Sample</u>	<u>% Blank</u>	<u>Found</u>	<u>Theoretical</u>	<u>%</u>
0	100	0	0	
25	75	120	119	101
50	50	260	238	110
75	25	390	355	110
100	0	475		

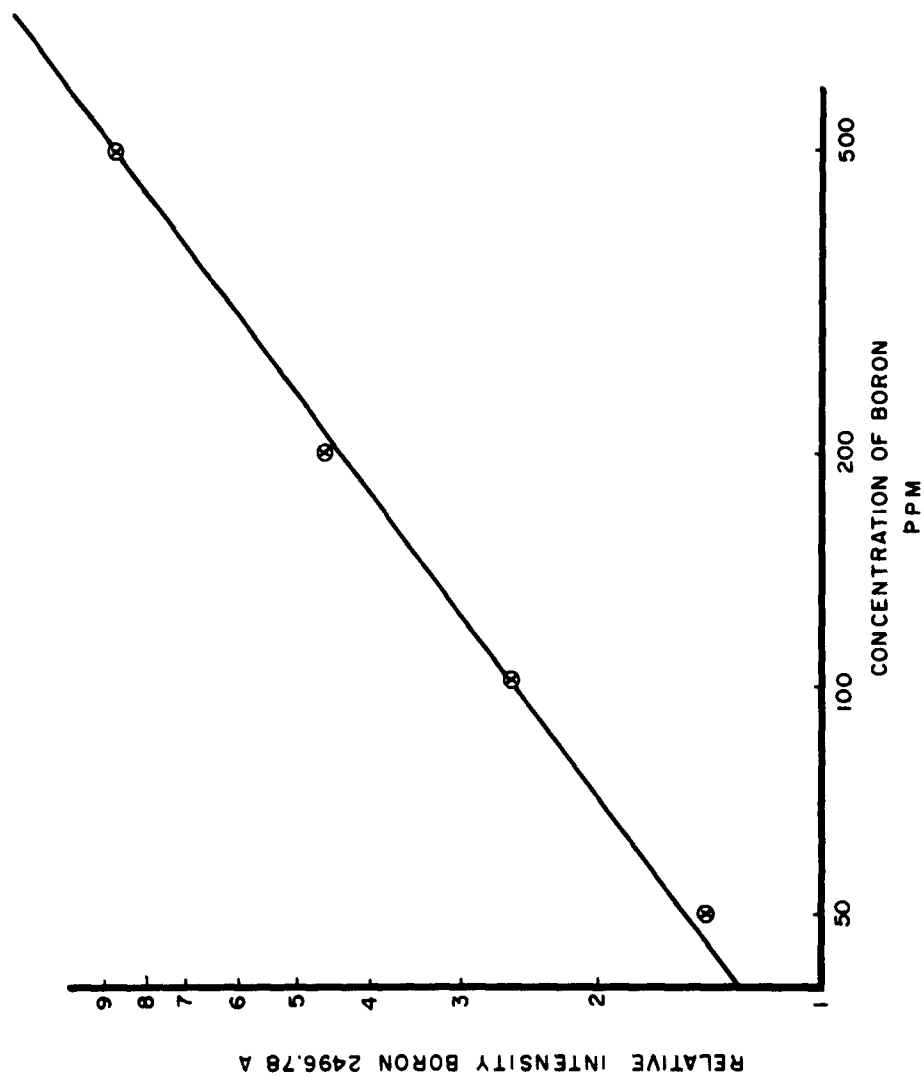


Figure 1. Analytical Curve - Boron in Molybdenum

LIST OF REFERENCES

1. Anderson, R. F., A General Chemical-Spectrographic Method for the Determination of Boron in Iron and Nickel-Base Alloys, *Applied Spectroscopy* 14, 123 (1960).
2. Dyck, R. and Veleker, T. J., Spectrographic Analysis of Molybdenum Metal Powder, *Anal. Chem.* 31, 1640 (1959).
3. Feldman, C., Evaporation of Boron From Acid Solutions and Residues, *Anal. Chem.* 33, 1916 (1961).
4. Mürau, P. C., Dissolution of Tungsten by Hydrogen Peroxide, *Anal. Chem.* 33, 1125 (1961).
5. Paterson, J. E. and Grimes, W. F., Spectrographic Determination of Boron and Silicon in Low-Alloy Steel by Fluoride Evolution, *Anal. Chem.* 30, 1900 (1958).

Aeronautical Systems Division, Dir/Materials
and Processes, Physics Lab, Wright-Patterson
AFB, Ohio.
Rpt No. ASD-TTR-63-290. THE SPECTROCHEMICAL
DETERMINATION OF BORON IN MOLYBDENUM. Final
report. Apr 63. 8p. incl illus., tables, 5
refs. Unclassified Report

A method for the spectrochemical determina-
tion of boron in molybdenum is described.
The method provides for the determination of
boron in the 50 to 500 ppm range by a carrier-
distillation technique with a precision of
±10 per cent.

(over)

1. Spectroscopy.
optical emission
2. Chemical analysis
3. Boron
4. Molybdenum
5. Heat-resistant
metals and alloys
- I. AFSC Project 7360.
Task 736005
- II. J. H. Muntz
- III. Aval fr OTS
- IV. In ASTIA collec-
tion

Aeronautical Systems Division, Dir/Materials
and Processes, Physics Lab, Wright-Patterson
AFB, Ohio.
Rpt No. ASD-TTR-63-290. THE SPECTROCHEMICAL
DETERMINATION OF BORON IN MOLYBDENUM. Final
report. Apr 63. 8p. incl illus., tables, 5
refs. Unclassified Report

A method for the spectrochemical determina-
tion of boron in molybdenum is described.
The method provides for the determination of
boron in the 50 to 500 ppm range by a carrier-
distillation technique with a precision of
±10 per cent.

(over)

1. Spectroscopy.
optical emission
2. Chemical analysis
3. Boron
4. Molybdenum
5. Heat-resistant
metals and alloys
- I. AFSC Project 7360.
Task 736005
- II. J. H. Muntz
- III. Aval fr OTS
- IV. In ASTIA collec-
tion